Synthesis of Phenylenedithiodiquinones

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The reaction of *o*-, *m*-, and *p*-benzenedithiol with 1,4-benzoquinone and with 1,4-naphthoquinone affords diquinones linked by a phenylenedithio moiety.

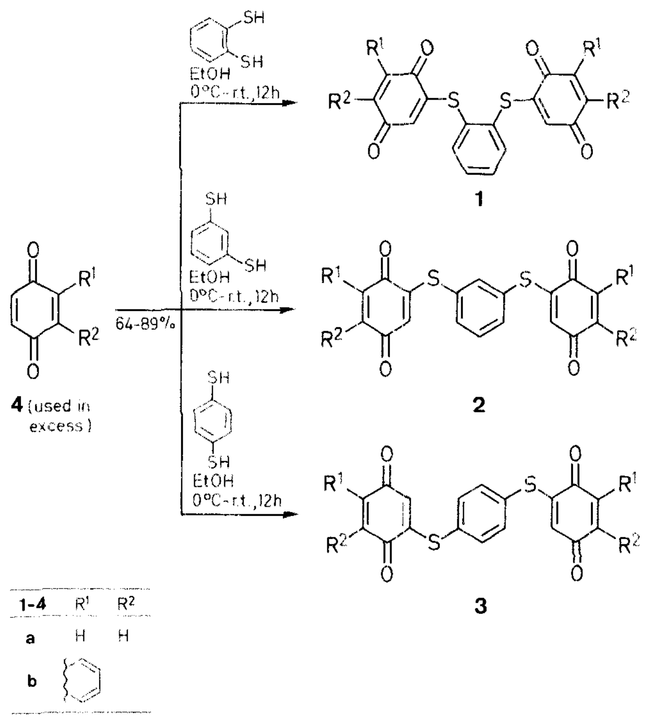
Considerable interest in polyquinoids and derivatives thereof stems from the assumption that with appropriately designed systems composed of quinone-, semiquinone-, and hydroquinone-type moieties, one could control optical, magnetic, and electrical properties.[1,2]

As part of an effort towards organic conducting materials we have designed and prepared compounds which contain linked donor(D) and acceptor(A) moieties as schematically represented by **I** and **II**.[3,4]

D---s---A---s---D **I** A---s---D---s---A **II**

s = spacer

We now report the synthesis of the isomeric templates **1**, **2** and **3** in which two acceptors (quinones) are linked by one donor (phenylenedithio), i.e., systems of the type **II**. Such A_2D molecular units are potentially endowed with a number of properties which are considered to be necessary for electrical conduction in organic charge-transfer complexes.[5] Compounds **1a**, **2a**, **3a** and **1b**, **2b**, **3b** were prepared in good yields by reaction of 1,4-benzoquinone (**4a**) or 1,4-naphthoquinone (**4b**), respectively, with *o*-, *m*-, or *p*-benzendithiol in ethanol at 0 °C to room temperature. The quinones are used in excess in order to oxidize the phenylenedithiobis(hydroquinones) which are initially formed by addition of the dithiols to the quinones.[6]



In the ^{1}H-NMR spectrum, the introduction of the phenylenedithio moiety causes a large upfield chemical shift for the adjacent quinonic proton ($\delta = 5.9-6.1$) as compared to $\delta = 6.7$ in 1,4-benzoquinone and $\delta = 6.9$ in 1,4-naphthoquinone). This effect might be due to resonance participation by the sulfur substituent. The other protons are not influenced. As common with monosubstituted 1,4-benzoquinones, compounds **1a**, **2a**, and **3a** show a typical ABC pattern with coupling constants $J = 2.3$ and 10 Hz.

The steric relationship between the two quinone moieties within the molecule has an effect on the physical and spectral properties of the isomers **1**, **2**, and **3** (Table).

Crystal structure and electrochemical properties of compounds **1**, **2**, **3** are currently under investigation.

1,2- and 1,3-Benzenedithiol are commercially available (Aldrich). 1,4-Benzenedithiol was prepared by reaction of 1,4-dibromobenzene with sodium 2-propanethiolate in EtOH and cleavage of the resultant 1,4-bis(isopropylthio)benzene with sodium according to Lit.[9] We failed to obtain this compound by a reported multistep synthesis from sulfanilic acid.[7,8]

Table. Products **1**, **2**, and **3** Prepared

Product	Yield[a] (%)	mp (°C)	Molecular Formula[b]	MS[c] *m/z* (%)	IR (KBr)[d] ν(cm^{-1})	UV(CH_2Cl_2)[e] λ_{max} (nm), (log ε)	^{1}H-NMR ($CDCl_3$/TMS)[f] δ, J(Hz)
1a	89	108–109	$C_{18}H_{10}O_4S_2$ (354.4)	354 (M^+, 100) 248 (54)	1665, 1638, 1566, 1545	248 (4.21), 430 (3.44)	5.91 (d, 2H, $J = 2.8$); 6.69 (dd, 2H, $J_1 = 2.8$, $J_2 = 10.2$); 6.86 (d, 2H, $J = 10.2$); 7.53 (s, 4H)
1b	69	>270	$C_{26}H_{14}O_4S_2$ (454.5)	454 (M^+, 100)	1662, 1588	259 (4.52), 297 (4.04), 400 (3.33)	6.01 (s, 2H); 7.66–8.12 (m, 12H)
2a	80	172–173	$C_{18}H_{10}O_4S_2$ (354.4)	354 (M^+, 100) 215 (84)	1662, 1641, 1567, 1545	250 (4.37), 421 (3.49)	5.92 (d, 2H, $J = 2.8$); 6.72 (dd, 2H, $J_1 = 2.8$, $J_2 = 10.2$); 6.86 (d, 2H, $J = 10.2$); 7.62–7.72 (m, 4H)
2b	79	262–263	$C_{26}H_{14}O_4S_2$ (454.5)	454 (M^+, 100)	1662, 1652, 1588, 1560	257 (4.66), 295 (4.19), 404 (3.69)	6.15 (s, 2H); 7.71–8.16 (m, 12H)
3a	82	210 (dec)	$C_{18}H_{10}O_4S_2$ (354.4)	354 (M^+, 100) 187 (42)	1667, 1641, 1564	259 (4.31), 424 (3.32)	5.96 (d, 2H, $J = 2.4$); 6.69 (dd, 2H, $J_1 = 2.4$, $J_2 = 9.8$); 6.74 (d, 2H, $J = 9.8$); 7.63 (s, 4H)
3b	64	>270	$C_{26}H_{14}O_4S_2$ (454.5)	454 (M^+, 100) 268 (26)	1661, 1648, 1588, 1565	257 (4.65), 291 (4.25), 405 (3.71)	6.21 (s, 2H); 7.71–8.20 (m, 12H)

[a] Yields of isolated products, not optimized.
[b] Satisfactory microanalyses: C ±0.22, H ±0.05, S ±0.24.
[c] Recorded on a Finnigan 4020 quadropole spectrometer.
[d] Recorded on a Nicolet 5DX FT-IR spectrometer.
[e] Recorded on a Bauch and Lomb spectronic 2000 UV/VIS spectrophotometer.
[f] Recorded on a Bruker WP200SY spectrometer.

Melting points were taken with a Thomas-Hoover capillary apparatus and are uncorrected.

2,2′-(1,2-, 1,3-, or 1,4-Phenylenedithio)bis(1,4-benzoquinones) 1a, 2a, 3a and 2,2′-(1,2-, 1,3-, or 1,4-Phenylenedithio)bis(1,4-naphthoquinones) 1b, 2b, 3b; General Procedure:

To a cooled (0 °C) solution of the quinone **4a** or **4b** (20 mmol) in EtOH (75 mL), a solution of 1,2-, 1,3-, or 1,4-benzenedithiol (0.569 g, 4 mmol) in EtOH (10 mL) is added dropwise, with stirring. The orange solution is stirred at r.t. for an additional 12 h, then cooled to 0 °C. The precipitated yellow to orange crude product is isolated by suction and recrystallized from EtOH (**1a, 2a, 3a**) or from CH_2Cl_2/petroleum ether 40–60 °C (**1b, 2b, 3b**) to give the pure yellow to orange crystalline product.

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